

Infrared Reflectance Spectrum of CaTiO₃ Calculated from First Principles

An important route to progress in wireless communications is the development of microwave dielectrics with improved properties and lower costs. Understanding the structure–property relationships of these technologically important materials will lead to the rational design of new materials with desired properties. Infrared reflectivity is an important tool for characterizing such materials because the IR reflectance spectrum is closely related both to the dielectric properties and to the atomic scale structure. Materials for microwave dielectrics, such as those based on CaTiO₃, have complicated crystal structures and thus complicated infrared spectra. This work shows that the IR reflectance spectrum of CaTiO₃ can be computed from first principles density functional theory, and can be interpreted in terms of the structure and chemistry of CaTiO₃.

Microwave dielectrics are used as resonators and filters in applications such as wireless communications. Microwave dielectric materials must have: (1) high dielectric constant ϵ' , (2) low dielectric loss, and (3) temperature stability. BaZn_{1/3}Ta_{2/3}O₃ (BZT), currently in use, has excellent properties but contains the expensive metal tantalum. The development of lower-cost, next generation, devices will require a replacement for BZT.

Fundamental knowledge of structure–chemistry–property relationships in dielectric materials will help achieve this goal. Current empirical knowledge of structure–property relationships in dielectrics is insufficient for the rational design of new materials. First-principles (FP) calculations complement experiment and are ideally suited for studying the physics of dielectric materials because they allow the origin of their physical properties to be studied on an ion-by-ion basis.

CaTiO₃ (CT) (Figure 1) is an important material for microwave dielectrics because it has very high dielectric constant ϵ' (approximately 180 at room temperature) and a positive temperature coefficient. By combining CT in solid solutions with materials with negative temperature coefficients, a large variety of potentially useful, zero temperature coefficient, materials can be obtained.

The dielectric constant of a material as a function of frequency ν is given by

$$\epsilon(\nu) = \epsilon_{\text{elec}} + \sum_{\mu} S_{\mu} \nu_{\mu}^2 / (\nu_{\mu}^2 - \nu^2 + i\gamma_{\mu}\nu), \quad (1)$$

where ϵ_{elec} is the electronic contribution to ϵ , the sum is over phonon modes μ , S_{μ} are the phonon oscillator

strengths, ν_{μ} their frequencies, and γ_{μ} their damping coefficients. The oscillator strength of phonon μ , in turn, is proportional to Z_{μ}^{*2}/ν_{μ}^2 , where Z_{μ}^{*} is the phonon's effective charge. Note that the number of phonon modes in Eq. (1) is determined from the crystal structure (25 in the case of CT), while Z_{μ}^{*} and ν_{μ} are determined by the crystal chemistry.

The dielectric constant as a function of frequency can be measured in many ways. Infrared reflectivity is a very useful, though indirect, method. Infrared reflectivity measurements are commonly fit using equation (1) to determine the phonon parameters. This becomes difficult, however, for a system as complicated as CT.

Alternatively, one can use FP methods to *compute* the phonon and dielectric properties, and thus the IR reflectance spectrum. Advances in FP methods have made it possible to compute Z_{μ}^{*} and ν_{μ} of a crystal, given as input only the experimental unit cell and atomic positions. The ability to correctly compute Z_{μ}^{*} is a relatively recent development and has led to the discovery that large Z_{μ}^{*} are common in perovskites, which enhances their dielectric constants.

Because of the technological importance of CT, and its strongly temperature-dependent ϵ' , collaborators at the Czech Academy of Sciences used IR reflectivity to explore the temperature dependence of ϵ' in terms of the temperature dependence of the phonon properties.

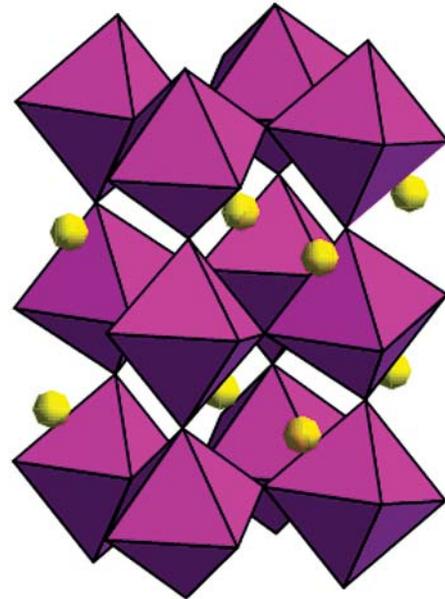


Figure 1: Perovskite-type structure of CaTiO₃. Ti ions are at the centers of oxygen octahedra, which are joined at their corners. Ca ions (yellow) occupy special positions between the octahedra.

The experimental IR reflectance spectrum at $T = 6$ K is shown in Figure 2. The IR reflectance spectrum that we calculated from FP is shown for comparison. (Although calculation of the damping parameters from FP is not yet practical, simply setting all γ_μ to the same value of 5 cm^{-1} leads to good agreement with experiment in this case.)

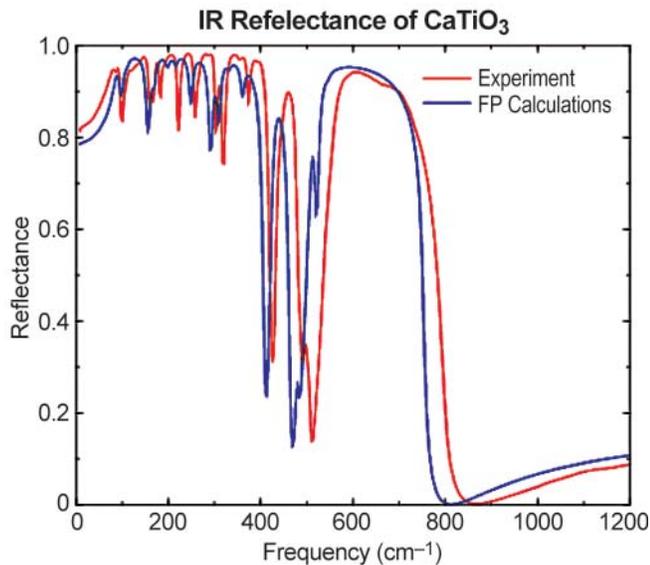


Figure 2: Comparison of the experimental infrared reflectance spectrum of CaTiO_3 with that computed from first principles. (Experimental results courtesy of V. Zelezny.)

Except for a systematic shift of the FP results toward slightly lower frequencies, the agreement between the two spectra is excellent. The results clearly demonstrate that FP calculations are able to compute IR reflectance spectra for perovskite-type oxides such as CT.

Given the accuracy of the FP calculations, it becomes possible to interpret the IR spectrum in terms of crystal structure and chemistry in unprecedented detail. In fact, a number of unexpected results were found. Many of these concern the importance of the tilting of the oxygen octahedra. If the oxygen octahedra were not tilted, only 3 phonon triplets would contribute to the dielectric function of CT, instead of the 25 modes for CT with octahedral tilting. Previous interpretations of the IR reflectance spectrum of CT were based on fitting the results to a 3 phonon model. However, the FP results show that it is impossible to correctly fit the experimental results with only 3 phonons, because the oscillator strengths of some of the modes that arise due to octahedral tilting are *larger* than those associated with the ideal perovskite structure. The three sets of phonons associated with the ideal perovskite structure have frequencies of approximately 80 cm^{-1} , 220 cm^{-1} , and 550 cm^{-1} , respectively. However, the modes near 160 cm^{-1} that arise due to octahedral tilting have higher oscillator strength than those near 220 cm^{-1} and are more dominant in the spectrum.

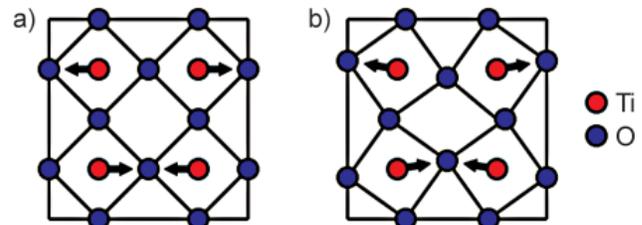


Figure 3: A phonon mode which is (a) nonpolar in the perovskite structure with untilted octahedra becomes (b) polar upon octahedral tilting.

One of the most significant features in the spectrum is the deep dip in reflectivity near 400 cm^{-1} . This feature arises due to the octahedral tilting as shown in Figure 3. In one of the normal modes of vibration of a perovskite, the atoms that are in the centers of oxygen octahedra (Ti for CT) vibrate out of phase with each other (Figure 3(a)). When the octahedra are tilted (Figure 3(b)), the same normal mode now has a net in-phase motion of Ti ions along one direction. In-phase motion of charged ions leads to a nonzero mode effective charge Z^*_μ and thus a contribution to the dielectric constant and IR reflectance spectrum.

An issue particularly relevant to industry is the temperature dependence of dielectric constants. Here, too, FP calculations have led to insight into the connection between the structure of CT and its rapidly decreasing dielectric constant as a function of temperature. FP calculations show that the large dielectric constant of CT is dominated by the contributions of the low-frequency phonons, which have both high Z^*_μ and low ν_μ . The large Z^* of these modes is due to the nature of the vibration. The Ti vibrate against the oxygen octahedra, while the Ca vibrate in-phase with the Ti. Experimentally, one finds that ϵ' decreases as temperature increases because the frequencies of the lowest-frequency phonons increase. The structure of CT also changes as the temperature increases. In particular, the oxygen octahedra tilting angles decrease. FP calculations on the phonon frequencies as a function of octahedral tilting show that the frequencies increase as octahedral tilting decreases, in agreement with experiment. The increase in phonon frequency can be explained by the shortening of Ti-O bonds as tilting decreases and the sensitivity of Ti-O force constants to bond length.

For More Information on this Topic

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V. Zelezny, E. Cockayne, J. Petzelt, M.F. Limanov, D. Usyat, V.V. Lemanov, and A.A. Volkov, "Temperature Dependence of Infrared-Active Phonons in CaTiO_3 : A Combined Spectroscopic and First Principles Study," submitted to *Physical Review B*.